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RESEARCH AND DEVELOPMENT PROGRAM ON THE USE OF COUNTING TECHNIQUES

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16. Abstract

The primary emphasis of this program was to reduce noise encountered in the multiplier of a quadrupole mass spectrometer when operating in an ion counting mode. This was to be done without sacrificing ion counting and collection efficiency. To this end, the use of an offset multiplier was investigated as a means of reducing certain elements of noise. In addition, two types of multipliers have been investigated in order to obtain the maximum stable signal-to-noise (S/N) ratio using ion counting techniques. A cold-cathode ion source/quadrupole mass spectrometer was again used as a test instrument for these investigations.

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SUMMARY

This program is a continuation of work performed under contract NAS1-5347, Task 8. The primary emphasis of this program was to reduce noise encountered in the previous studies, without sacrificing ion counting and collection efficiency. To this end, the use of an offset multiplier was investigated as a means of reducing certain elements of noise. In addition, two types of multipliers have been investigated in order to obtain the maximum stable signal-to-noise (S/N) ratio using ion counting techniques. A cold-cathode ion source/quadrupole mass spectrometer was again used as a test instrument for these investigations.

An off-axis arrangement for the ion counting electron multiplier has been designed and tested which has practically eliminated the photon noise background encountered in the previous work. In addition, a new electron multiplier has also been investigated which has two orders of magnitude more gain than the original multiplier. The resultant ion counting detector is nearly insensitive to large changes in overall multiplier gain. For instance, a factor of seventy change in dc gain of the multiplier resulted in a change in the average counting sensitivity of less than 12%. Thus the overall sensitivity of the detector is much more stable.

Finally, it appears that the ion detector can be made less sensitive to other properties of the ions emerging from the quadrupole such as mass, energy and possibly exit angle. As a result, the counting ion detector appears to approach the ideal of a low noise level, stable means of detecting ions from mass spectrometers, total pressure gauges and other charged particle devices.

INTRODUCTION

In a previous program report (ref. 1), the use of counting techniques was investigated to improve the S/N ratio of an UHV mass spectrometer employing a cold-cathode ion source (CCIS) and a quadrupole analyzer. During these investigations the most prominant noise source was traced to photons emanating from the cold-cathode discharge. Similar problems have been described (refs. 2 and 3) in connection with hot-filament quadrupole spectrometers. In fact, all line-of-sight analyzers (time-of-flight, quadrupole, coincidence, etc.) are theoretically prone to this source of noise. Although the photon background in the CCIS is pressure dependent (unlike the hot filament source), it was decided to improve the S/N ratio of the CCIS/Quad by using an off-axis detector. The resolved ion beam is electrostatically deflected off-axis prior to entering the electron multiplier, while the photons pass by largely undetected.

In addition to the photon noise background problem, it was discovered that the electron multiplier then in use did not have sufficient gain to guarantee freedom from sensitivity changes caused by multiplier gain instabilities. From the data available it appeared that the minimum gain required to detect the ions with present equipment was approximately 10^6 (for 4 KeV ions). In order to allow for substantial changes in multiplier gain, which is a common problem, an initial gain near 10^8 was sought. Thus, after a substantial change, the remaining gain would be sufficient to guarantee counting stability. This goal and that of photon noise reduction appears to have been largely reached in the present program.

The selection of an appropriate multiplier for use in this work is not entirely straightforward. Since the resolved ions emerge from the quadrupole at relatively large angles, consideration must be given to this factor in selecting an appropriate multiplier. Moreover, the chosen multiplier must be selected from a noise standpoint since its inherent thermionic noise forms a lower limit of detectability for the system. These factors are also considered and discussed.

Finally, the use of ion counting detectors alters the quantitative interpretation of spectral peak heights as compared to dc detection methods. Limited discussions of this subject are also presented.

LIST OF SYMBOLS AND ABBREVIATIONS

B	magnetic field (gauss)
CCIS	cold-cathode ion source
CCIS/Quad	cold-cathode ion source/quadrupole
cpm	counts per minute
cps	counts per second
Disc.	discriminator setting (volts)
eV_{ax}	axial component of ion energy (volts)
eV_{tr}	transverse component of ion energy (volts)
I_c	collector current (amperes)
I_K	CCIS total cathode current (amperes)
m	mass
MBAG	Modulated Bayard-Alpert Gauge
P	pressure (Torr)
pps	pulses per second
Res.	resolution setting (arbitrary units)
r_o	radius of circle inscribed within quadrupole rod structure (meter)
S	detector sensitivity (pulses per second/Torr)
S/N	signal-to-noise ratio
UHV	ultra high vacuum (pressure $< 10^{-9}$ Torr)
V_A	anode potential (volts)

V_D	deflector voltage (volts)
V_M	multiplier voltage (volts)
V_R	retarding potential (volts)
ϕ	exit aperture angle (radians)
ω	rf angular frequency (radians per second)

RESEARCH AND DEVELOPMENT PROGRAM ON THE USE OF COUNTING TECHNIQUES

Program Goals and Objectives

Scope of Present Program. - The present program is a continuation of work begun under contract NAS1-5347, Task 8 (ref. 1). In this previous program, the use of ion counting techniques was investigated as a means of improving the S/N ratio of an UHV residual gas analyzer. While this effort did result in S/N ratio improvements, it was recognized that two additional steps were necessary in order to achieve the optimal improvement. First, the most prominent noise source encountered was identified as photons emanating from the ion source of the instrument. Similar problems have been encountered in hot-filament ion source mass spectrometers. In the latter instruments however, the photon noise is independent of pressure. In contrast, the CCIS photon noise is largely pressure dependent and therefore S/N ratio does not deteriorate as noticeably at very low pressures. Thus, by making the ion counting detector "photon blind", a higher S/N ratio is theoretically achievable with the CCIS/Quad. For this reason, the present program was devised and the effect of photon noise reduction was investigated.

A second advantage of the use of ion counting techniques is that a major improvement in detector stability is possible. This fact was investigated in the previous work and it was found that the electron multiplier gain was insufficient to permit a substantial improvement in detector stability. Thus, a second objective of the present work was to demonstrate improved detector stability with a more appropriate multiplier. This goal has also been accomplished as will be shown herein. Thus the scope of the present program is to improve the detector S/N ratio and to improve the stability of the detector through the use of ion counting techniques. The cold-cathode ion source/Quadrupole mass spectrometer is again used as a test instrument for the investigations reported herein.

"Photon-Blind" Ion Detectors

Methods and Arrangements. - A number of different types of electron multipliers are described in the literature. Some of these have been specifically adapted to the general problem of signal-to-noise ratio improvement. Others could conceivably be so adapted. For instance, the resistance strip multiplier (refs. 4 and 5) (with and without a magnetic field) have been developed and extensively tested as ion detectors. In theory, such devices can be geometrically arranged so that photons will transit the space between the two strip-like secondary emission surfaces without releasing enough secondary electrons to contribute significantly to the background noise. In contrast, the ions would be electrostatically deflected so that they strike the entrance portion of the strip and thus produce sufficient secondaries to provide the desired charge gain for ions. In practice, the success of this method depends heavily on certain details of the geometrical arrangement.

In another arrangement, a conventional focused dynode multiplier, which would normally be responsive to photons, is located off-axis to the emerging ion/photon beam. Again, the ions are electrostatically deflected to the first dynode whereas the photons (noise) largely miss the entrance to the dynode structure. Other workers (refs. 2 and 3) have used this arrangement with success to avoid the photons emerging from a conventional quadrupole spectrometer.

Finally, in an adaptation of familiar scintillation counting techniques, other investigators (refs. 6 and 7) have developed and tested such techniques in an effort to eliminate the gain instability of multipliers caused by unpredictable contamination from the vacuum environment. This method also effectively separates photons and ions although this advantage is not specifically described and discussed.

In summary, three alternative arrangements can be used either singly or in combination, to separate photon noise from the resolved ion beam. These are briefly:

1. Use of photon transparent (strip) multipliers.
2. Off-axis deflection of ions into conventional multipliers.
3. Use of scintillation techniques to provide both photon separation and improved multiplier gain stability.

Before discussing the selection of an appropriate multiplier and the chosen arrangement for photon noise reduction, the properties of the ion beam emerging from the quadrupole will be discussed. These properties strongly influence both the selection of the multiplier and the adaptation of the multiplier to the quadrupole.

The energy with which ions leave the quadrupole is low compared to the energy required for useful secondary emission ratios at the first dynode of the multiplier. The exit aperture angle for the resolved ions can, however, be very large depending on many interrelated parameters such as mass, frequency and phase of the rf voltages on the quadrupole, injection energy, quadrupole length, etc. Thus, the emerging ions are not only distributed over some energy range but are also distributed over a wide range of angles. As a result, focusing of the emerging "beam" at the detector is difficult for all angles and energies simultaneously, especially if an unreasonably small detector is chosen. If the collection efficiency of the detector is substantially less than 100%, complicated mass discrimination effects can occur at the detector (ref. 2). Since one of the purposes of the present work is to reduce the influence of the multiplier on the overall instrument sensitivity, it is apparent that the multiplier and its adaptation to the quadrupole must be accomplished with some care. The next section will discuss the choice of suitable multipliers.

Selection of Suitable Electron Multiplier

Characteristics of Idealized Multiplier. - From the foregoing discussions and certain conclusions drawn from the previous work (ref. 1), the pertinent characteristics of an idealized multiplier may be summarized as follows:

1. The minimum gain for ions should be > 1×10^6.
2. The multiplier should be insensitive to photons (if possible) in the visible and soft x-ray (< 100 eV) regions.

3. The multiplier should accept the large angular spread of ions from the quadrupole without appreciable loss in collection efficiency.

4. The total dark current noise from the multiplier (thermionic emission, field emission and leakage) should be small at the highest gain available; an acceptable figure is 10 cps at a gain of 10^8.

5. The pulse height distribution for noise and ions should be as narrow as possible and the average ion pulse height should be appreciably larger than the average noise pulse height.

6. The multiplier gain should be as stable as possible and should be independent of both the counting rate (up to approximately 10^6 cps) and the total number of events counted.

7. The secondary emission ratio at the first dynode (or input surface) should be as insensitive to entrance angle as possible.

8. The dynode material, or secondary emission surfaces, should be as insensitive to repeated exposures to room air as possible and should be bakeable to 400°C without damage.

9. In situ measurement of multiplier gain is desireable although not absolutely necessary.

10. The device must be compatible with good UHV practice (low outgassing rates).

11. The multiplier should achieve the desired gain without resorting to very high voltages (> 4 kV) which accentuate field emission problems.

12. The multiplier should be as insensitive to stray magnetic fields as possible.

13. The multiplier should not produce spurious pulses which can be detected as signal (ion) pulses.

With the above criteria in mind, a number of multiplier types were surveyed for use with the CCIS/Quad. In addition to the resistance strip and focused dynode types, the channel multipliers were also considered. These types have three very desirable characteristics, namely: high initial gain (10^8 or greater), narrow pulse height distribution (in the saturated mode), and low dark current. Of the various types of channel multipliers commercially available, only those equipped with an entrance cone were considered appropriate for reasons discussed previously in connection with the focusing of the emergent ion beam.

The channel multipliers were not selected for laboratory study for the following reasons: (a) The reported fatiguing effects (refs. 8 and 9) as a function of counting rate and total counts, (b) relatively small entrance area for the cone-equipped units and (c) the maximum recommended bakeout temperature is 300°C.

The resistance strip multipliers were also not chosen because the maximum available gain is insufficient to insure the desired detector stability. For gains in excess of 10^7, ion feedback causes spurious after-pulses. A gain near 10^8 is desirable to insure better detector stability for large gain changes.

The choice of multipliers was therefore narrowed to the focused dynode types. The 14 stage BeCu dynode multiplier used in previous studies was again used in the preliminary study phase of the present program, primarily because of large amount of dc and pulse S/N data had been collected using this multiplier. The initial gain of the multiplier was approximately 10^7. For the experiments reported herein, the gain was about one order of magnitude lower.

A very high gain (10^8) multiplier was purchased and installed in the CCIS/Quad in both the on-axis and off-axis configurations. The performance with this multiplier is described in later sections.

Description of Apparatus and Equipment

Vacuum System. - The vacuum system used was essentially the same as that used in the previous studies (ref. 1). This system consists of two manifolds, each of which is pumped by a small (20 L/sec) ion pump. The upper manifold contains a Modulated Bayard-Alpert gauge (MBAG), the CCIS/Quad and the ion pump, together with a connecting UHV valve. During baking, all parts of the upper manifold are baked (including the ion pump). The "lower" manifold and pump are used to evacuate the upper manifold during this procedure. Ultimate true pressures in the low 10^{-12} Torr region have been achieved using this procedure. The lower manifold contains suitable valves for admitting test gases. The UHV valve between the upper and lower manifold serves as both an isolation valve and as a variable leak for admitting test gases.

CCIS/Quadrupole Spectrometer. - A complete description of all previous work conducted on the CCIS/Quadrupole including previous studies on the use of ion counting techniques appears in the referenced report (ref. 1).

Ion Counting Equipment. - Preliminary studies were made using the counting equipment described in the previous report. The majority of present studies were made using more versatile electronics which included the following:

a. Preamplifier with fixed voltage gains of 10 and 100. Designed to amplify photomultiplier pulses and to operate with the equipment listed below.

b. Scaler-Timer - 200 nsec resolving time. Preset time or preset count. Variable discriminator (0.025 volts to 5.0 volts). Integral or differential count modes with wide or narrow window widths (ΔE).

c. Digital to Analog Converter - 3 Digit Selection.

d. Spectrum Scanner - 50, 100 and 200 channels. Scans the full pulse height interval of the scaler timer. Used to obtain integral or differential pulse height distributions on X-Y recorder.

Experimental Procedures and Results

Baseline Experiments. - Before experimental studies of the off-axis multiplier were begun, baseline experiments were conducted to establish a reference noise background for the instrument under a controlled set of conditions.* A prepared mixture of the inert gases (He, Ne, Ar, Kr, and Xe) was admitted to the spectrometer which was operated under a prescribed set of resolution and sensitivity conditions. Both the dc and counting rate S/N ratio were measured. The total pressure of the inert mixture was determined by a Modulated Bayard-Alpert Gauge (MBAG). The UHV system and MBAG were given a thorough bakeout and outgassing to reduce the influence of residuals on the background noise.

Attempts to obtain this baseline information were not completely successful. First, contamination from either nitrogen or carbon monoxide (mass 28) and also hydrogen (mass 2) was noted, each contributing to the background noise to an unknown extent. Second, difficulty was encountered with external noise sources such as rf pick-up, line noise, and amplifier noise. Normally the latter two sources do not contribute significantly to noise observed between mass peaks. These noise elements were encountered when the amplifier gain and discriminator level were set to obtain a counting efficiency approaching 100%. As a result, the 100% counting efficiency point could not be clearly defined and the absolute gain could not be measured.** The in-

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* The photon noise background is dependent on both the molecular species and the partial pressure thereof.

** Refer to ref. 1, pages 68 and 114 for gain calculation methods.

ference was however, that the multiplier gain had deteriorated since previous investigations, although this supposition could not be proven.

Photon Noise Reduction. - In the previous work (ref. 1), it was found that the substitution of a tubular cathode stub (in the ion source) for a solid one of the same diameter and length, improved the S/N ratio of the instrument substantially. As viewed from the multiplier end of the quadrupole, only the small annular area of the stub remained visible. It was decided to attempt an additional improvement in S/N ratio by flaring the end of the tube, so that its annulus would be completely invisible to the multiplier. This modification was made and its effect on S/N ratio was examined briefly. A spectrum of nitrogen (N_2^+ and N^+) was taken under conditions nearly identical to those of Fig. 30 of the previous report (ref. 1). The discriminator was set to obtain a photon background count of 31 counts per minute (cpm) at 5.5 amu. The observed nitrogen peak counting rate at mass 28 was 6×10^5 cpm. The counting S/N ratio obtained with the flared cathode stub was 2×10^4. This ratio is essentially the same as that observed in the previous work. It is concluded, therefore, that the flaring of the open end of the tubular cathode study did not improve the counting S/N ratio to any measurable extent.

Other Noise Sources. - During the investigation of the flared cathode stub, the multiplier dark current was observed to increase in a spontaneous manner after a weekend of pumping. Prior to this event no dc multiplier dark current was detected at a multiplier operating potential of 2000 volts. A small ion source background current of 1 x 10^{-13} amperes was also observed in the output of the multiplier. After the unknown change, the multiplier dark current increased to 7 x 10^{-13} amperes at the same multiplier voltage. Four days later, this value had increased to 3 x 10^{-12} amperes. The photon or ion source noise current subsided to a value < 1 x 10^{-13} amperes as a result of the continued pumping. The residual peaks were also substantially diminished as a result of the extended pumping.

On a pulse counting basis, the situation was completely reversed; i.e., the multiplier background pulses could not be detected at the minimum discriminator setting of 0.025 volts* and with 3700 volts applied to the multiplier. Photon pulses from the ion source were readily identifiable (approximately 25 counts/sec) under these conditions.

The fact that the multiplier background was clearly definable on a dc basis but not a pulse basis, suggested the possibility of a leakage current. The multiplier dynode and collector elements are mounted on two ceramic insulators. The dynodes are therefore electrically coupled to the electron collector (output) through these insulators. A simple calculation of the typical leakage resistance required of the ceramics shows that a total resistance of 2 x 10^{16} ohms is necessary to limit the leakage current to 1 x 10^{-13} amperes with 2000 volts applied to the multiplier. This form of noise is readily identified by a measurement of the linearity of the noise current with applied voltage (over a limited range). This measurement

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*Minimum detectable pulse amplitude at the output of the preamplifier with voltage gain of 100. Actual minimum detectable pulse high at input to amplifier is 0.25 millivolts.

was made and it was demonstrated that the multiplier noise was not of the simple ohmic variety. The measured multiplier background and ion source photon noise currents were observed to increase as a power function of the applied voltage for a range of 1500 to 3700 volts. The rate of increase of these currents with applied voltage was not as large as the data shown in Fig. 31 (page 119) of the previous report (ref. 1) thereby confirming the speculated loss in gain.

The effect of this gain loss on the ion counting and ion collection efficiencies was investigated next. Specifically, it was demonstrated that the multiplier had sufficient gain (at 3700 volts) to detect nearly 100% of the ions of a given mass (mass 28). The minimum detectable pulse height was 0.25 millivolts under these conditions. The gain of the multiplier (for N_2 ions) was calculated from a dc measurement of the mass 28 peak amplitude and a counting rate equivalent of this peak which was known to represent nearly 100% counting efficiency. The gain thus measured at 3700 volts was 1.4×10^6. This is in contrast to a mass 28 gain measurements of 8.15×10^5 made at 3000 volts in the previous report (ref. 1, page 114). Thus, increasing the multiplier voltage from 3000 to 3700 volts resulted in a gain increase of only a factor of 1.7. On the basis of a conservative extrapolation of the gain curve shown in Fig. 31 of the previous report (ref. 1), it is estimated that the gain was originably 4-5 $\times 10^6$ at 3700 volts applied.

In summary, the performance of the multiplier immediately prior to its relocation off-axis was as follows:

1. The gain for mass 28 ions had decreased to a value such that an additional 500-600 volts was required to obtain full ion detection efficiency.

2. The background current of the multiplier had spontaneously increased to a value nearly ten times larger than the photon noise. Due to the decreased gain, this noise was not detectable on a pulse basis at the minimum discriminator setting of 0.025 volts.

3. The presence of ion source photons was still detectable, particularly at the higher multiplier voltages.

4. The photon background reference measurements made with a prepared mixture of inert gases were of reduced value due to the loss in gain and also the contamination of hydrogen and mass 28 discussed previously.

The next section will describe the first of two off-axis configurations employed and the results obtained.

Off-Axis Studies Using 14 Stage Multiplier

Mounting Details. - The multiplier described above was originally designed to be used with the EAI Quad 200 residual gas analyzer. In preparing it for the off-axis configuration, simple modifications were made. These modifications are shown in Fig. 1 using dotted lines to show the original parts removed. First, the focusing plate normally used to focus photoelectrons to the first dynode in a photomultiplier configuration was removed by cutting a single mounting rod. This leaves the first dynode and its focusing grid intact. Secondly, the original mounting bracket and output connection were carefully disconnected and removed. A new mounting bracket was substituted for the original one which reduced the overall length of the multiplier by one-half an inch. This provided the additional space needed to deflect ions into the entrance grid of the first dynode. These modifications were made in as clean an area as possible to prevent contamination and dust from entering the dynodes. Careful handling is essential to prevent contamination of the ceramic insulators by fingerprints which are impossible to remove after 400°C bakeout.

Electrostatic Deflector. - A pair of curved electrostatic deflector plates were provided to bend the beam off-axis. These parts were made of Nichrome V and mounted as shown in Fig. 1. The purpose of the electrostatic deflector is to bend the ion beam immediately prior to its acceleration by the first dynode grid. As will be shown later, the deflector worked well in guiding the beam to the vicinity of the first dynode grid. Although some loss of ions was anticipated, no serious loss of collection efficiency was observed.

Performance of Deflector System. - After assembling the multiplier in the off-axis configuration, the system was given a mild bakeout (250°C for 6 hours) and the performance of the ion deflector was investigated. Figure 2 shows the results.

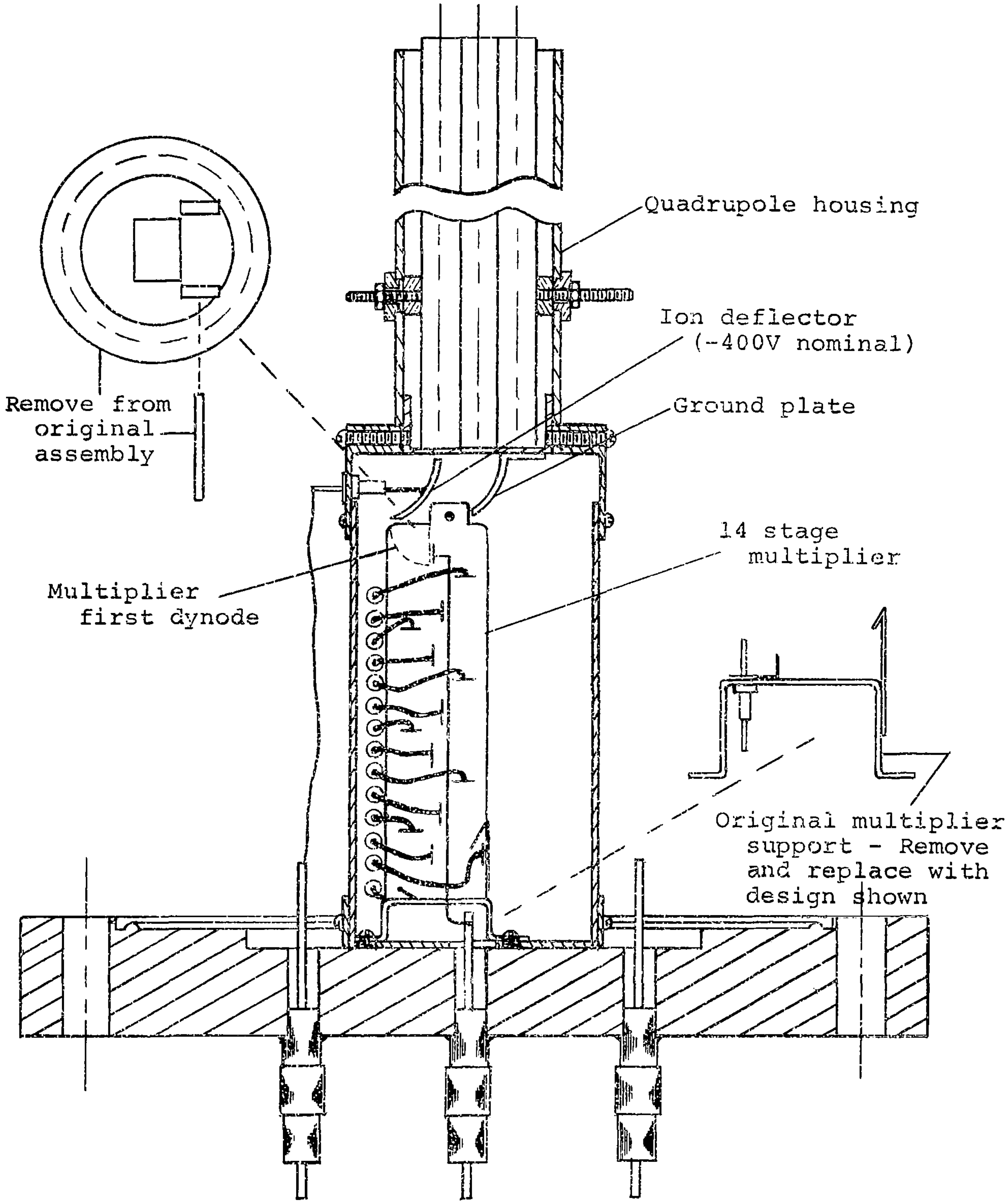

Figure 1.- 14 stage multiplier (off-axis configuration)

The quadrupole was set to "zero" mass, allowing all ions to transit the quadrupole. The deflector voltage was then varied with a fixed multiplier accelerating voltage (2000 volts in this figure). With the deflector potential negative (correct for ion deflection) a broad maximum in the multiplier output current was observed. With the deflector voltage of incorrect polarity (positive), the beam was driven to the grounded deflector plate, as was anticipated. Next, the multiplier voltage was increased from 2000 volts to 3000 volts. As was also anticipated, the deflector potential became less influential in guiding the ions to the first dynode because of the increased acceleration potential of the first dynode grid.

The foregoing evaluation of the deflector system was rather cursory because the quadrupole voltages (both ac and dc) were zero. With the quadrupole operating, the rf voltage imparts increased transverse energy to the ions. The axial energy component (eV_{ax}) remains unchanged throughout the quadrupole. As shown by Woodward & Crawford (ref. 10), the maximum transverse exit energy (eV_{tr}) is given by

$$eV_{tr} \approx \frac{m\, r_o^2 \omega^2}{8} \quad (1)$$

where e is the ionic charge, m is the ionic mass, r_o is the radius of the circle inscribed within the quadrupole rods, and ω is the rf angular frequency. Thus, at the higher mass numbers, the maximum exit aperture angle ϕ is expected to increase as

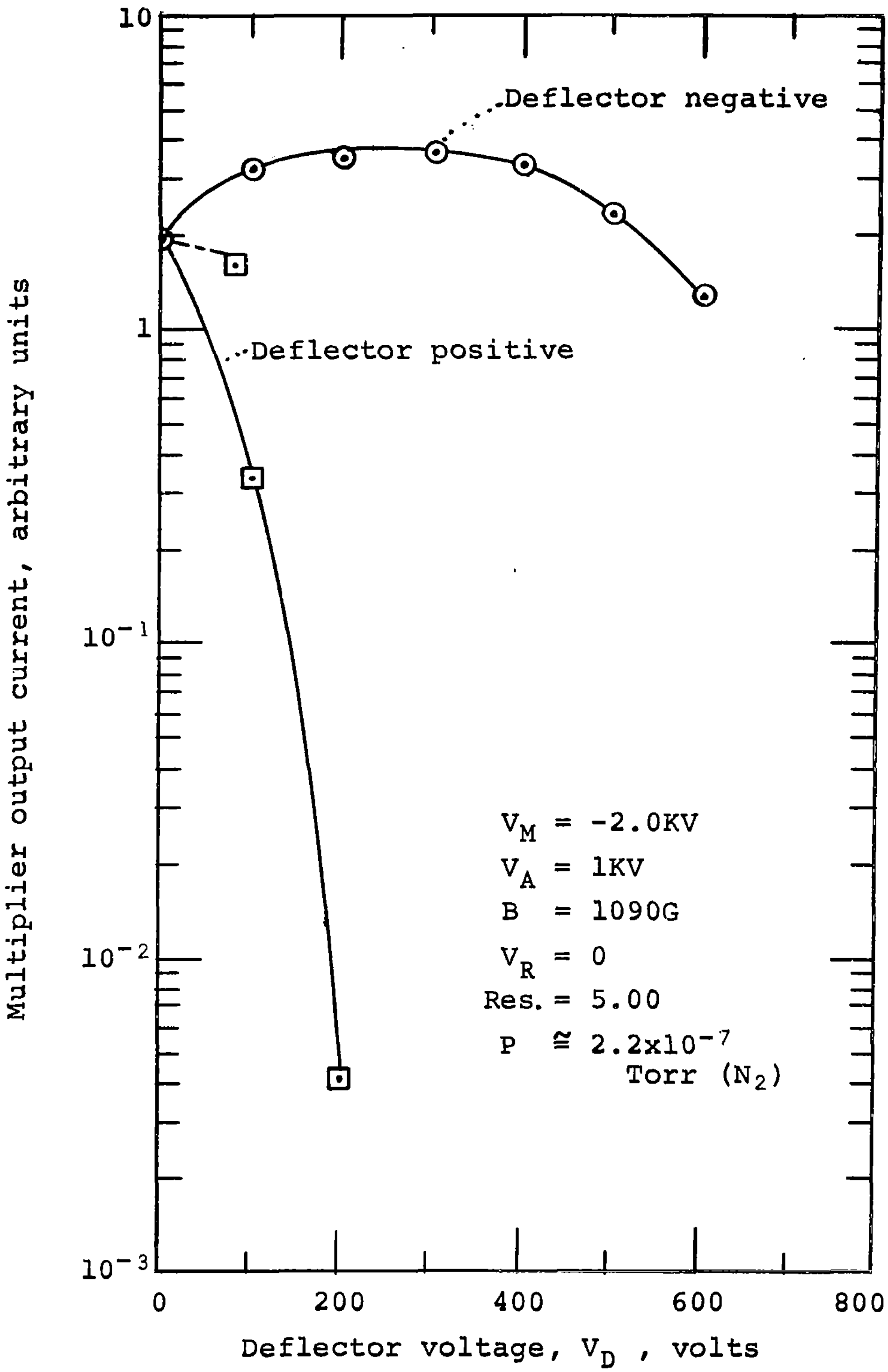

Figure 2.- Deflector characteristics (all ions)

$$\phi = \tan^{-1} \frac{V_{tr}}{V_{ax}}$$

$$= \tan^{-1} \frac{m\, r_o^2\, \omega^2}{8\, V_{ax}} \qquad (2)$$

Results of Off-Axis Studies. - After demonstrating the performance of the electrostatic deflector the spectrometer was pumped down to the UHV region. A photon background measurement was performed (as mass 5.5) prior to a planned S/N ratio measurement using the inert gas mixture. Figure 3 shows a typical analog residual gas spectrum taken at this time. Counting data are also given for selected peaks. The multiplier was operated at -3700 volts and the pulse height discriminator was again set to the minimum value of 0.025 volts. Under these conditions all nitrogen ions were being counted.

Two peaks were noted; one at mass 4 (He^+) and one at mass 6 (C^{++}). The proximity of the latter peak to the 5.5 amu noise point made readings at this point suspect. Mass 9.5 was chosen to avoid this problem, since no peaks were expected in the vicinity. A background count of 4 counts per sec was noted at this point. With the source off, the counting rate dropped to a few cpm, confirming the presence of photons or ions emanating from the source. The spectrometer was next operated under conditions which would cut off all ions to the multiplier. A very large retarding voltage was used to prevent ions from entering the analyzer. At the same time, the resolution of the spectrometer was set to infinity so that the transmission of all ions would be essentially zero. Under these conditions only photons and/or multiplier dark current would be measured in the output.

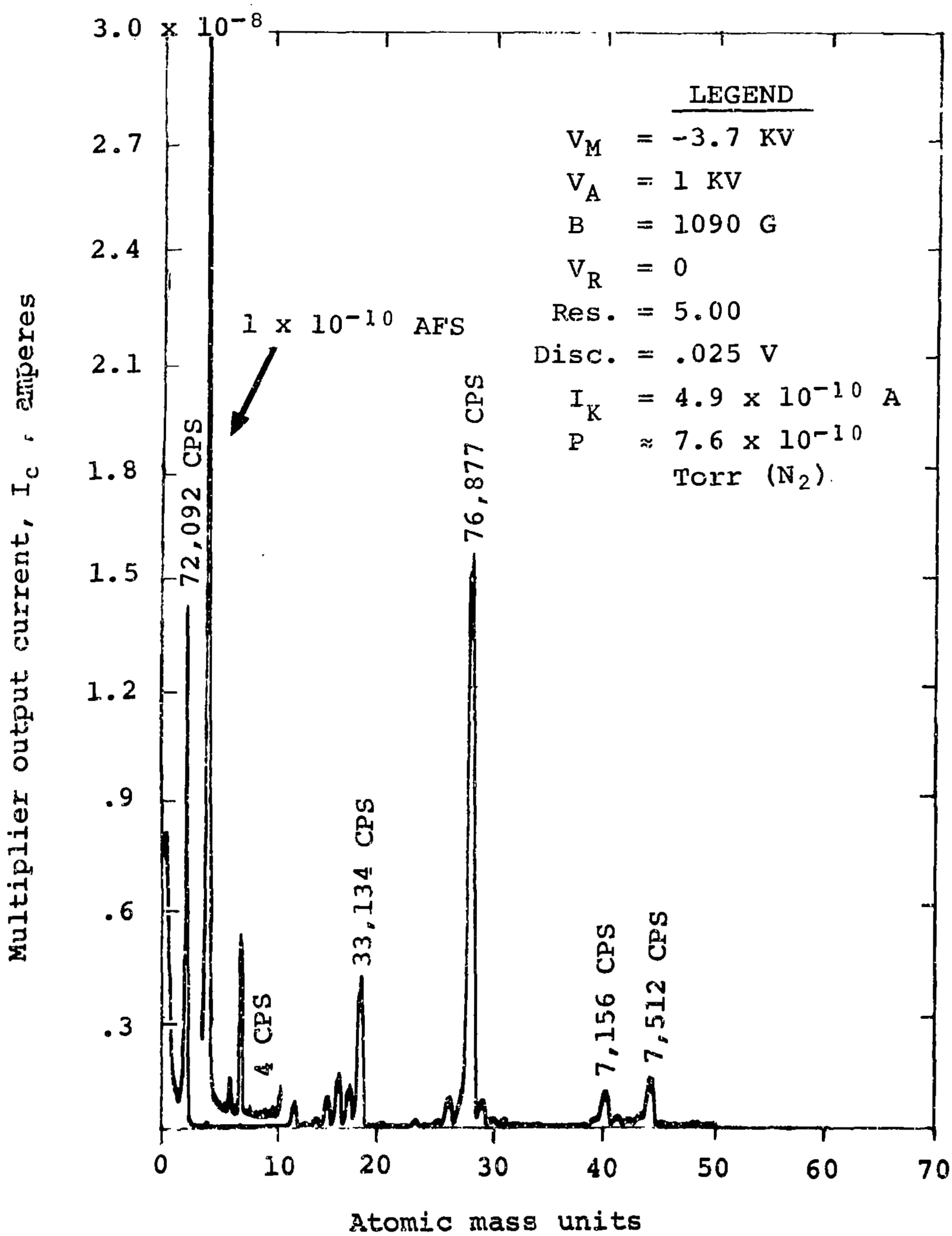

Figure 3.- Analog spectrum of residual gases with off-axis multiplier.

The only background current observed was traceable to the multiplier. On a pulse counting basis, the counting rate (few counts/minute) was statistically insignificant. No peaks were observed in a spectrum scan up to mass 35. It appears therefore that the counting rate observed at 9.5 amu was due mainly to ions, probably 19^{++} amu.

In an effort to determine the true photon background at mass 5.5, the spectrometer was baked at 400°C overnight. While the residual peaks in the vicinity of mass 5.5 were reduced, an exceptionally large multiplier dark current was encountered which was shown to be ohmic leakage between the electron collector and adjacent dynodes. The multiplier was removed and the surface of the ceramic insulators cleaned with pure ethyl alcohol. The multiplier was re-installed and the dark current measured. Before bakeout, the dark current was of the order of 5×10^{-13} amperes at 3000 V. A second bakeout was begun, after which an exceptionally large dc dark current of 9×10^{-10} amperes was observed. The multiplier was again removed, cleaned and re-installed. The system was not baked, but was continuously pumped for 13 days. At the end of this period, the residual peaks were sufficiently low to permit investigation of photon noise. The dark current pulses were observed with the minimum discriminator setting and 3700 volts on the multiplier. The observed total pressure (nitrogen) was 7.8×10^{-10} Torr. Under these conditions an average noise count was taken at mass 5.5 with and without the ion source operating. With the source operating the observed noise was 281.4 counts/minute. With the ion source off, the observed noise was 256.8 counts/minute. The net counting rate (for photons) was therefore 24.6 counts/minute, (0.41 counts/sec) at 7.8×10^{-10} Torr.

Because of the difficulties encountered with multiplier leakage currents (which were aggravated by baking), plans to standardize background measurements using the inert gas mixture were abandoned. Some comparisons can be drawn from previous data taken under nearly the same conditions. For example, Fig. 4 shows a nitrogen spectrum obtained previously with the multiplier on-axis. The average background rate at mass 5.5 is 162 counts/sec at a pressure of approximately 7×10^{-10} Torr. With the ion source turned off, the multiplier background was 16 counts/sec. Thus the net ion source background is only 0.41 counts/sec as described above. It appears from these data that a reduction of approximately 300 has been made in the photon background by locating the multiplier off-axis.

Because of the leakage deterioration of the multiplier further experiments with it were discontinued. A new, very high gain multiplier was substituted as will be discussed next.

Performance of High Gain Multiplier

<u>Preliminary Studies On-axis</u>. - The multiplier selected for this phase of the program was a Johnston Laboratories, Inc.

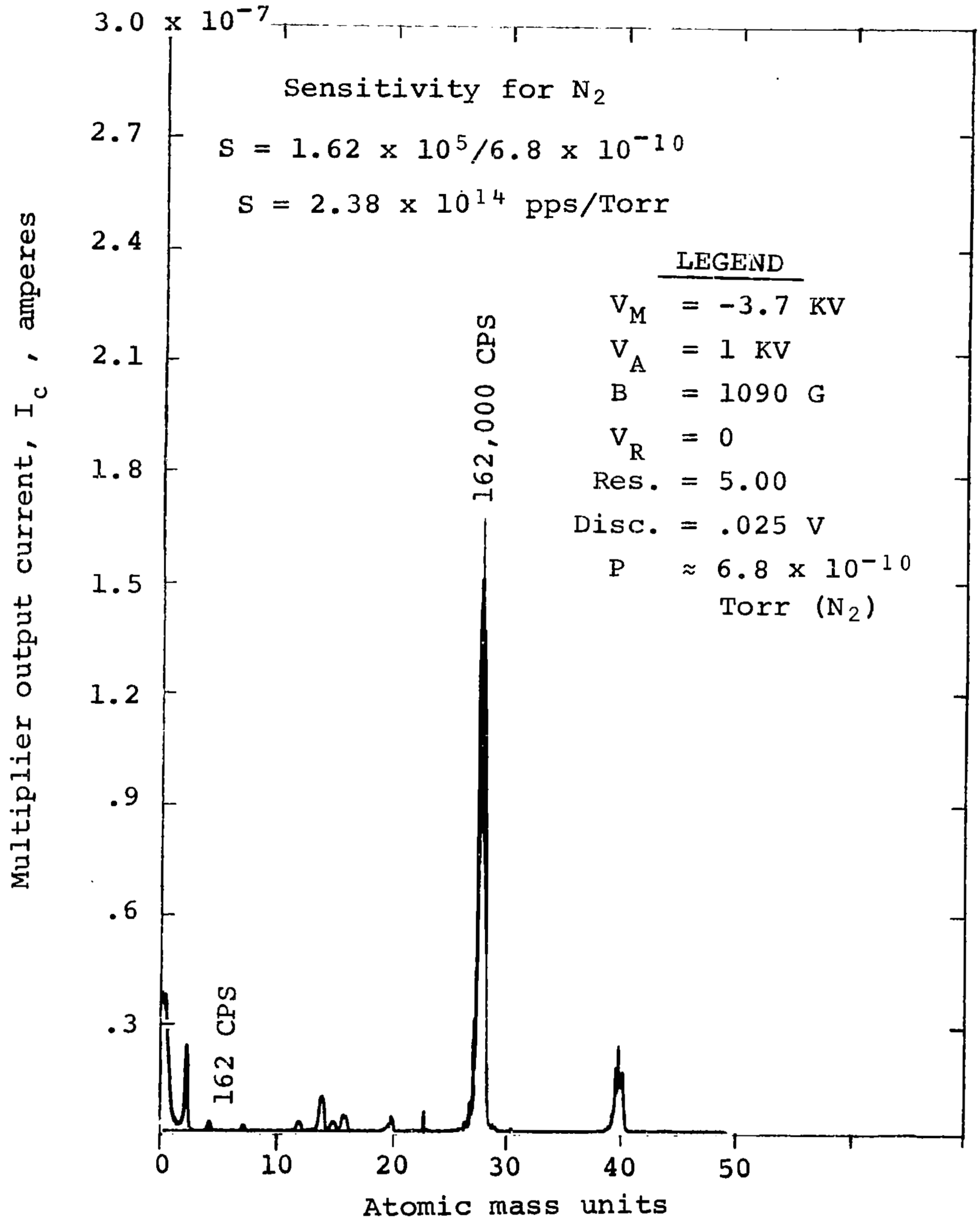

Figure 4.- Analog spectrum of nitrogen with on-axis multiplier.

Model MM-1 focused mesh multiplier employing 20 stages of electron multiplication. According to the data sheet supplied with the multiplier, its gain (for 700 eV electrons) was 1.3×10^7 at 2900 volts applied. Gain factors approaching 10^8 are advertised for applied voltages between 4.0 and 4.5 kV. The multiplier is not known to fatigue at high counting rates and is specified to have a dark current $< 10^{-13}$ amps at 10^6 gain ($<$ 1 electron per second).

The multiplier was first installed in the on-axis configuration shown in Fig. 5. The purpose of this work was to obtain a baseline for measuring off-axis reduction in the photon background. Shortly after beginning operation two difficulties were encountered; first, pick-up of the quadrupole rf frequency was detected at the minimum discriminator level and at mass numbers above approximately 20 amu. This difficulty was overcome by very careful shield grounding both inside the multiplier housing and at the outside of the main vacuum feed-through flange. Some difficulty was also encountered with dust particles between the dynodes which generated field emission noise when operating voltages $>$ 4.0 kV were applied. A sudden, large increase in background noise characterizes the onset of this problem. Careful handling of the multiplier in a cleanroom eliminated the problem.

Preliminary studies of the high gain multiplier began with an examination of ion and photon collection and detection efficiencies. Figure 6 will explain the purpose of these studies and describe the results. With the discriminator set at its

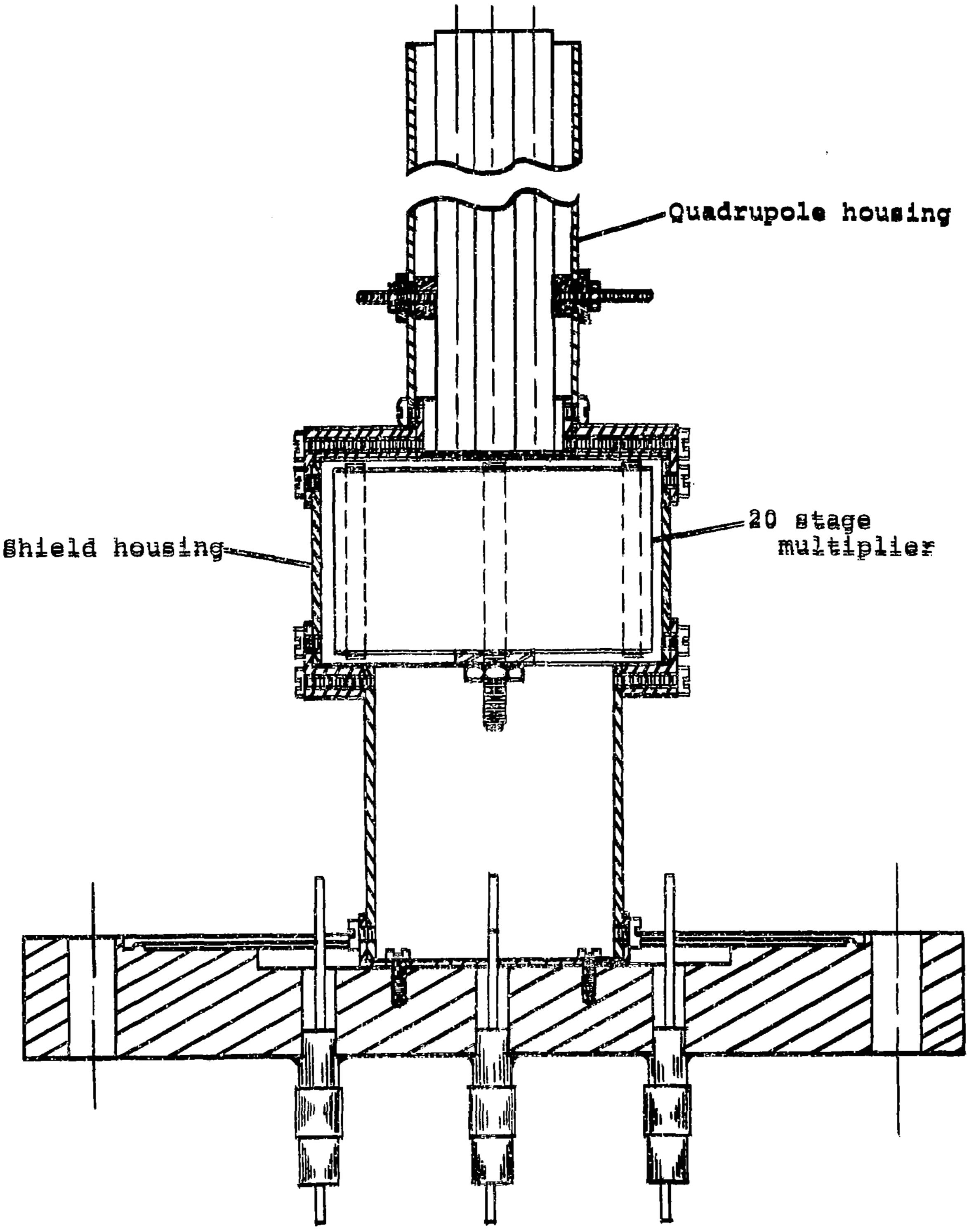

Figure 5.- 20 stage multiplier on-axis configuration

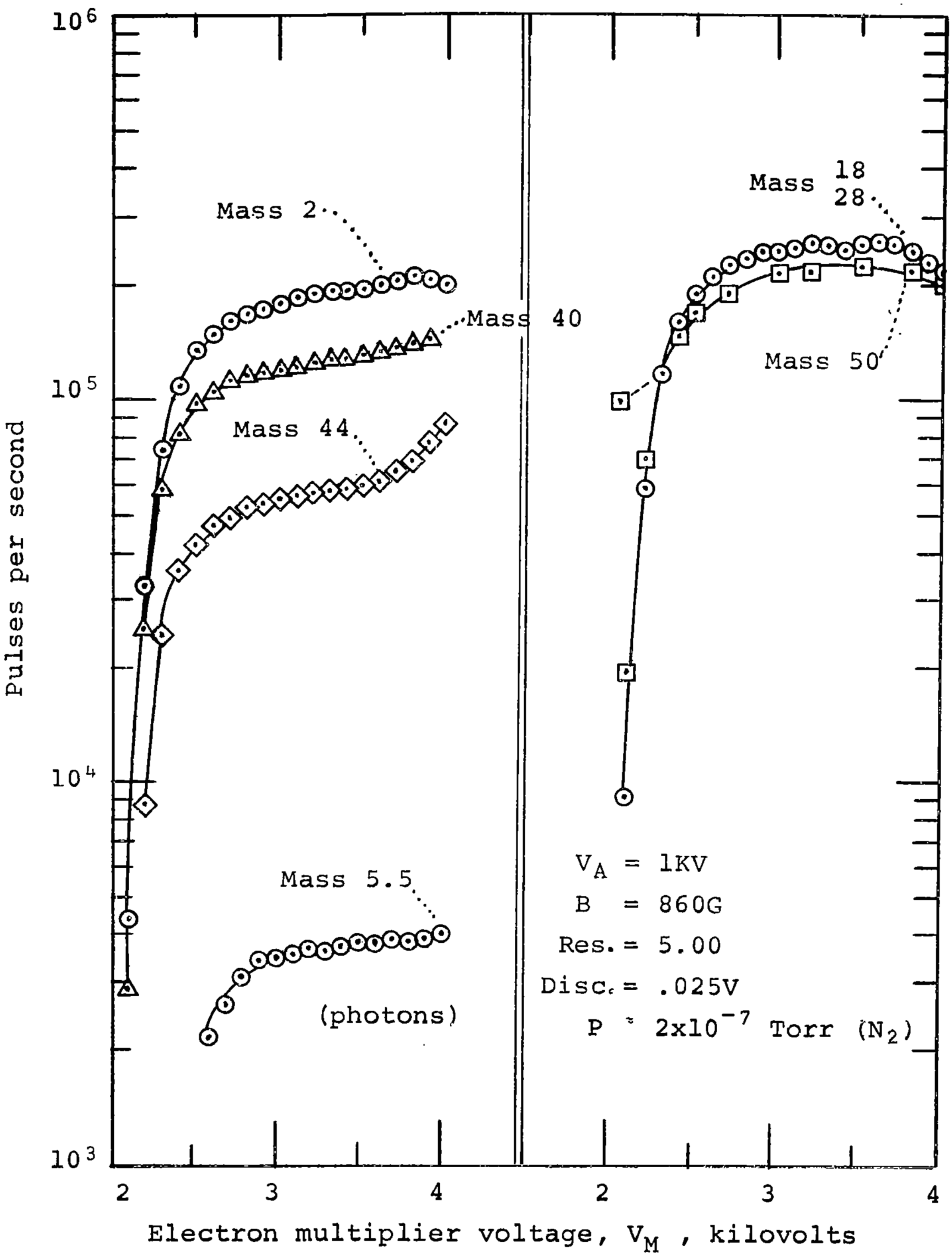

Figure 6.– Counting rate vs. multiplier voltage for selected masses

minimum level of .025 volts, the counting rate was measured as a function of multiplier voltage for photons at mass 5.5 and for ions at masses 2, 18, 28, 40, 44 and 50. It was anticipated that the ion and photon counting rate curves would reach a plateau as the multiplier voltage (gain) was increased. The onset of this plateau signifies that all pulses are larger than the minimum discrimination level. The photon curve shows this effect clearly for multiplier voltages > 3500 volts. Similarly, ions of masses 18, 28 and 50 also exhibit a plateau, albeit with other effects to be discussed shortly. For masses 40 and 44, the tendency to reach a counting plateau is followed by a noticeable increase in counting rate. This effect is probably due to desorption of these specific gases by electron bombardment within the multiplier. At higher voltages the electron flux in the later dynode stages increases sharply and gas desorption can occur. During the time this data was being taken the cathode current of the CCIS/Quad was monitored to detect changes in total ion source density. During the investigation of the Argon (40) and CO_2 (44) small but noticeable increases were observed in the ion source cathode current as the multiplier voltage was increased. This effect was not observed for the other gases. Presumably these gases were selectively desorbed by electron bombardment in the later dynodes of the multiplier, a portion of which returned to the ion source and was again ionized, analyzed and detected. The multiplier was originally shipped in a sealed container, back-filled with Argon. It is not surprising therefore that this is one of the gases involved.

It will be noted that the counting rate plateau for masses 2, 18, 28 and 50 decline between 3700 and 4000 volts. Upon further investigation, it was found (using an oscilloscope) that the largest pulses were overloading the pre-amplifier. The overload resulted in pulse overshoot which effectively deadens the amplifier during the overshoot period. As a result, other pulses were not being counted during the "dead" period and the counting rate declined. This type of counting error becomes more pronounced at higher multiplier gain and higher counting rates. This effect is separate and distinct from another cause of lost counts due to resolution losses in the counting circuit.* Counting losses due to overloading occur in the pre-amplifier, whereas resolution losses occur in the counting circuitry. Thus, in assembling or designing a set of electronics for ion counting, special attention must be given to the pre-amplifier which is typically required to amplify the broad pulse height distribution encountered in focused dynode multipliers. The pre-amplifier employed here will not overload on pulse outputs as large as 10 volts while providing a voltage gain of 100 for all pulses. This discussion indirectly emphasizes one of the advantages of the channel type multipliers, namely their narrow pulse height distribution (when operated in the saturated mode).

Finally, the tendency of a given counting system to overload will also depend on ionic mass. As will be discussed subsequently, the overall gain of the multiplier is approximately inversely related to mass. In general the lighter masses produce larger pulses than the heavier masses. Thus, this form of counting loss is typically more pronounced for the lighter masses.

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*See ref. 1, pages 84-86.

Gain stability measurements. - Figure 6 indicates that all ions of masses 2, 18, 28, 40, 44 and 50 are being counted for multiplier voltages between 2900 and 3900 volts. Thus, if a loss in multiplier gain occurs corresponding to a 1000 volt reduction in multiplier operating voltage only a minor reduction in counting rate for all masses between 2-50 amu would be expected. This is indeed the case, as is shown by Figs. 7 and 8. These figures are pulse counting spectra, i.e., they are digitally derived but recorded in analog form. Figure 7 was taken at a multiplier voltage of 3900 and Fig. 8 was taken at 2900 volts. The measured reduction in gain for mass 28 was a factor of seventy. On a counting rate basis, the corresponding reduction in sensitivity is much less, as is obvious from the two spectra. Table I below summarizes the percentage change in counting rates for some twenty species in the 2-50 amu range.

The percent change in counting rate is obviously higher for the higher mass numbers. Those masses displaying a percentage change greater than the average (-11.4%) occur with a greater frequency above mass 28 than below. It is well known (refs. 11 and 12) that mass discrimination effects occur in the electron multiplier because of variations of the secondary emission ratio with mass, energy, and composition. For low energy ions (few keV), the number of secondary electrons produced at the first dynode per incident ion varies inversely as the square root of the ionic mass. It is anticipated therefore that the gain of the multiplier will be generally lower for higher mass numbers. A given loss in multiplier gain will thus cause a greater reduction in counting rate at higher masses than at low, particularly if the original gain of the multiplier

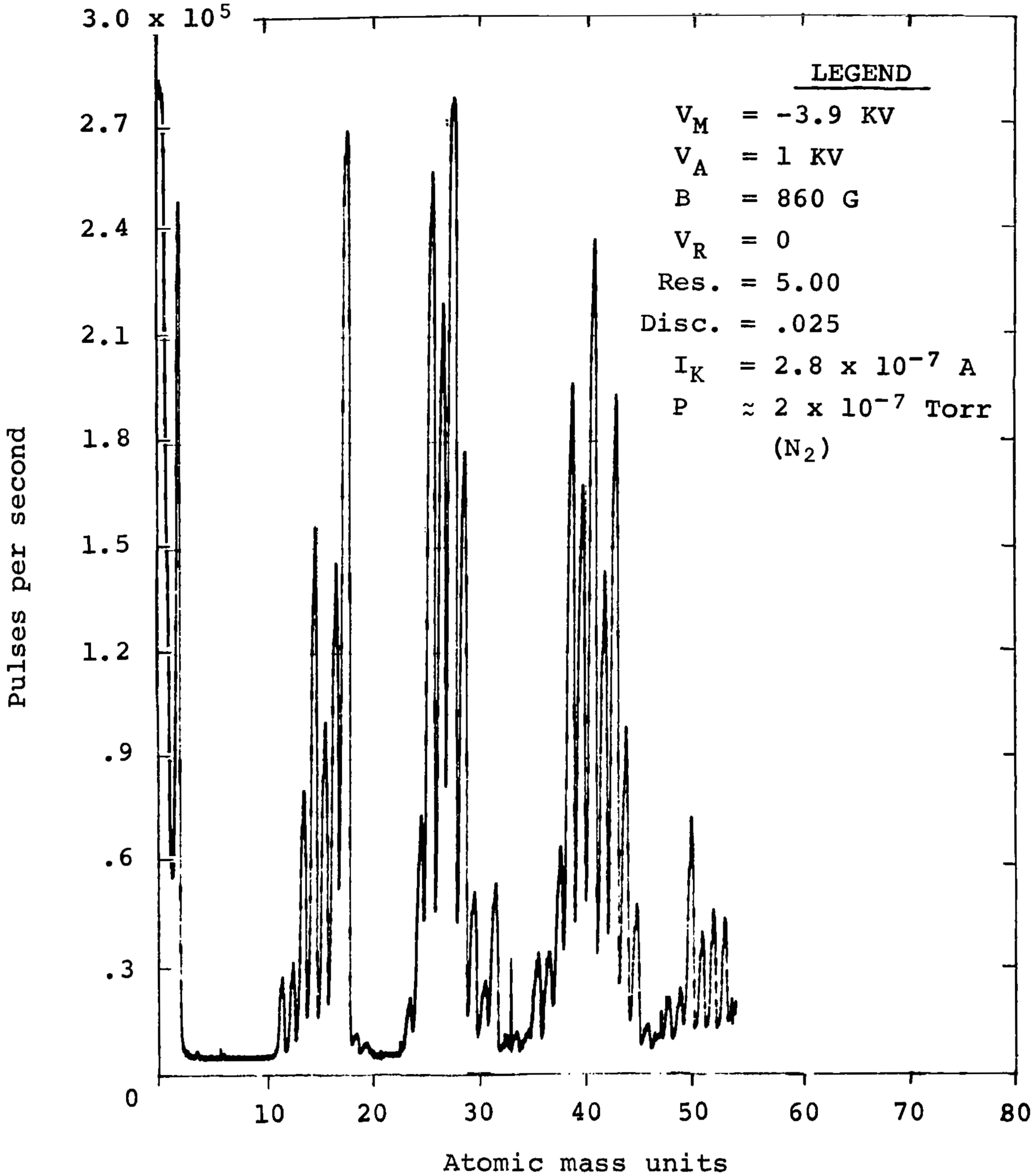

Figure 7.- Digital spectrum of residual gases with 20 stage on-axis multiplier at 3.9 KV.

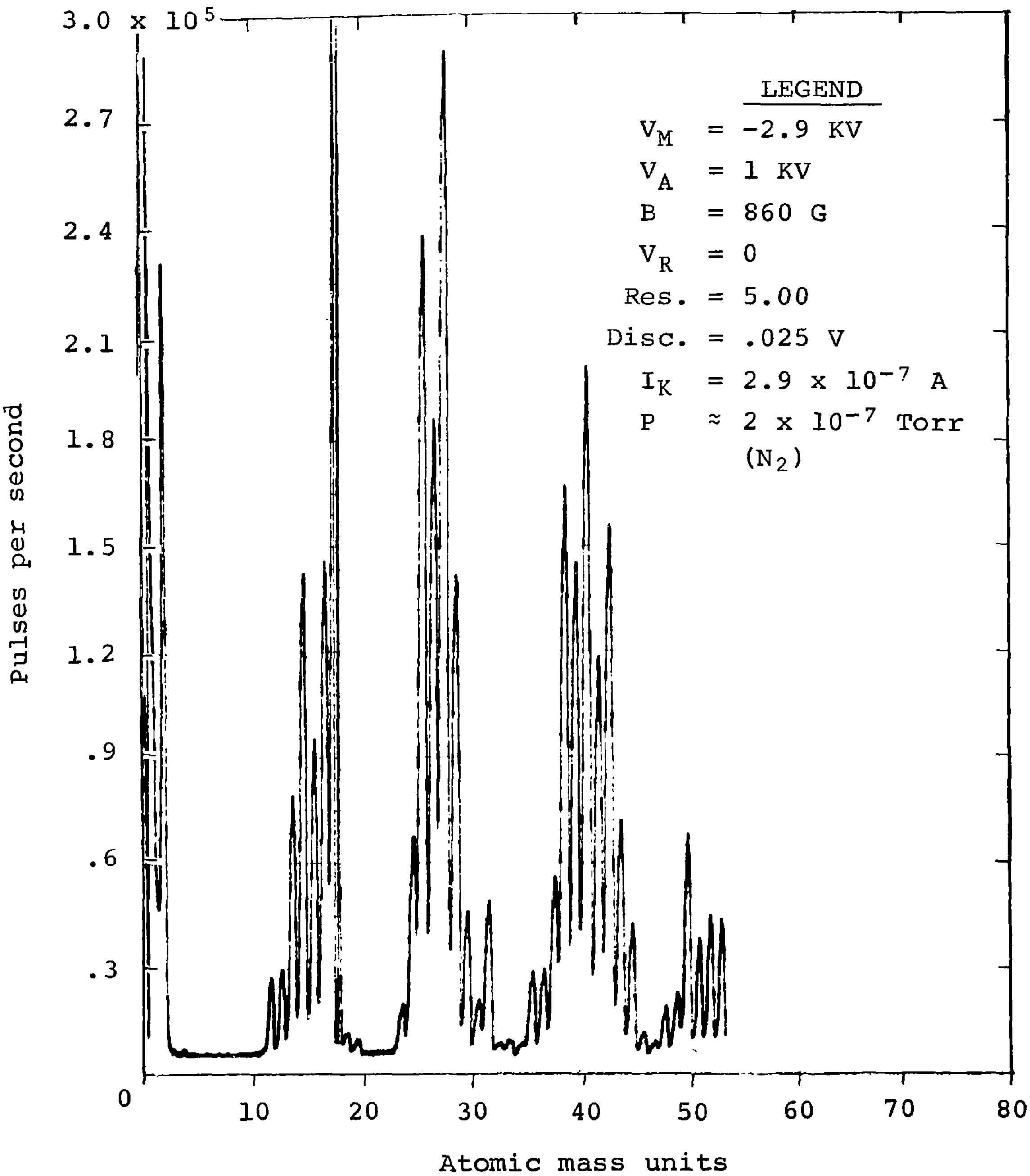

Figure 8.- Digital spectrum of residual gases with 20 stage on-axis multiplier at 2.9 KV.

TABLE I

PERCENT CHANGE IN COUNTING SENSITIVITY FOR SELECTED MASSES

Mass No. amu	Count Rate @ 3900 V x 2.5 x 10^5 cps	Count Rate @ 2900 V x 2.5 x 10^5 cps	Percent[a] Change
2	.81	.752	-7
12	.076	.073	-4
13	.090	.080	-11
14	.251	.246	-2
15	.50	.456	-9
16	.315	.30	-5
17	.470	.470	0
18	.878	Off Scale	-
24	.055	.048	-13
25	.228	.205	-10
26	.84	.777	-8
28	.908	.950	+5
29	.57	.45	-21
30	.156	.135	-13
32	.163	.145	-11
36	.100	.078	-22
38	.200	.168	-16
41	.772	.650	-16
42	.460	.376	-18
44	.310	.220	-29
50	.225	.206	-8

[a]Average of this column is 11.4%.

is near the minimum required for 100% counting efficiency. Table I verifies this statement, since the percentage reduction in counting rates for masses above 28 amu is generally larger than the corresponding reduction for masses less than 28 amu. Masses 24 and 50 are noted as exceptions.

At the same time the digital spectra of Figs. 7 and 8 were taken, analog spectra were also obtained for the same constituents and conditions. From these data, the multiplier gain as a function of mass can be calculated. This has been done for 3900 volt ions and is summarized in Table II below:

TABLE II

CALCULATED GAINS FOR SELECTED MASSES AT 3900 VOLTS

Mass No. amu	Gain (X 10^8)
2	3.7
14	0.7
18	2.4
28	3.2
40	0.7
44	0.56
50	0.60
53	0.58

We note the aforementioned lower gains for mass numbers above 28 amu with the singular exception of mass 14. Figure 9 shows the analog data used in conjunction with the digital data of Fig. 7 to calculate the above gain factors. The lower dc currents for all peaks above mass 28 are readily apparent when compared to the digital spectra of Fig. 7.

In summary, a notable improvement in the gain stability has been made using the high gain multiplier. For a very large change in multiplier gain (factor of 70 for nitrogen), a relatively small reduction in pulse counting sensitivity has occurred. It appears that the present multiplier approaches the idealized characteristics listed previously. A notable exception is the broad pulse height distribution which may lead to missed counts at high gain and high counting rates.

Off-axis Studies. - In the final phase of the program the high gain multiplier was mounted off-axis as shown diagrammatically in Fig. 10. A photograph of this installation is shown in Fig. 11. Three outer shield plates have been removed to show the multiplier and deflector plate.

The configuration (90° off-axis) is not necessarily an optimal arrangement for the multiplier. It was chosen because the relatively large size of the multiplier would not permit mounting inside the existing vacuum container at intermediate angles.

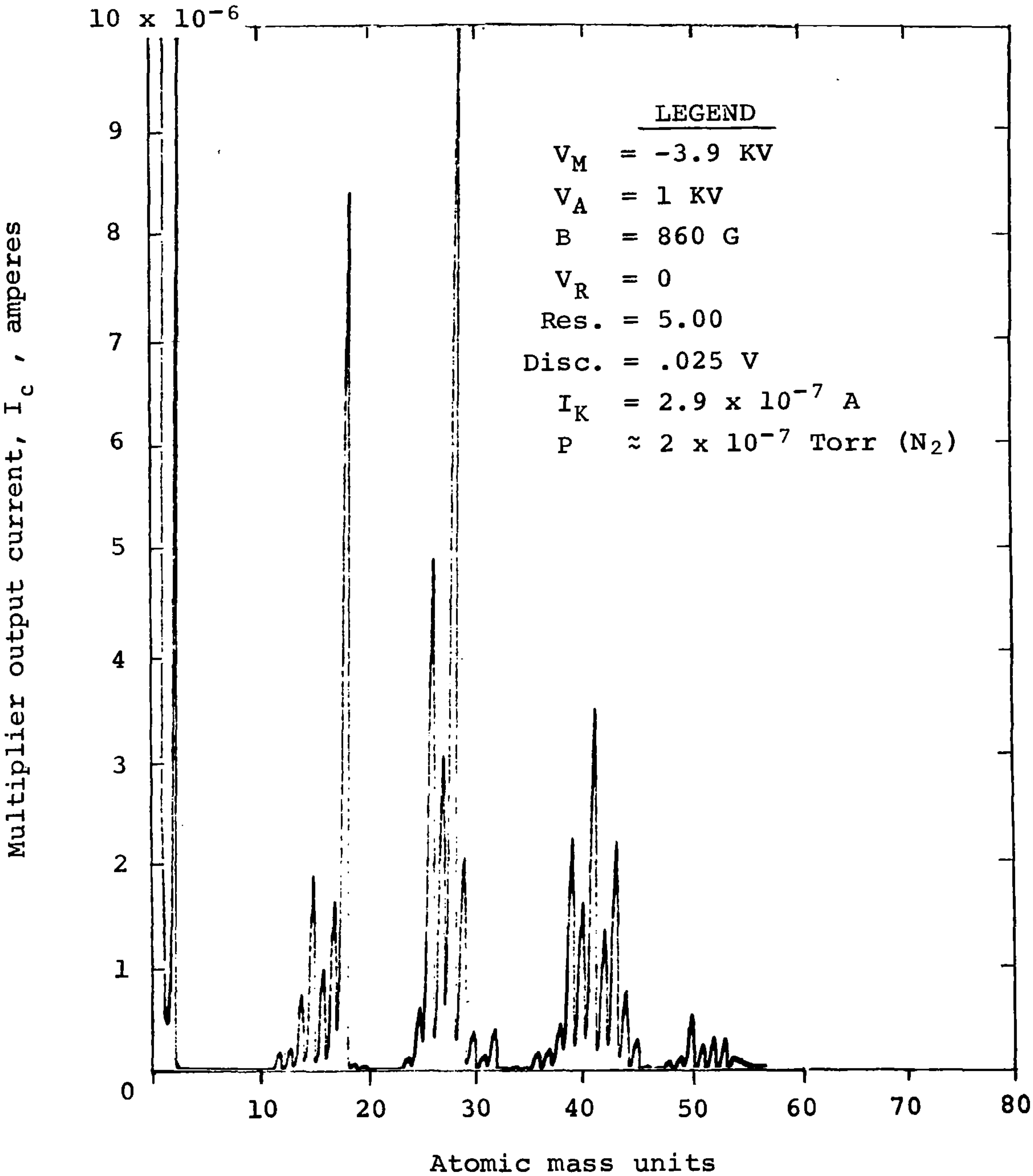

Figure 9.- Analog spectrum of residual gases with 20 stage on-axis multiplier at 3.9 KV.

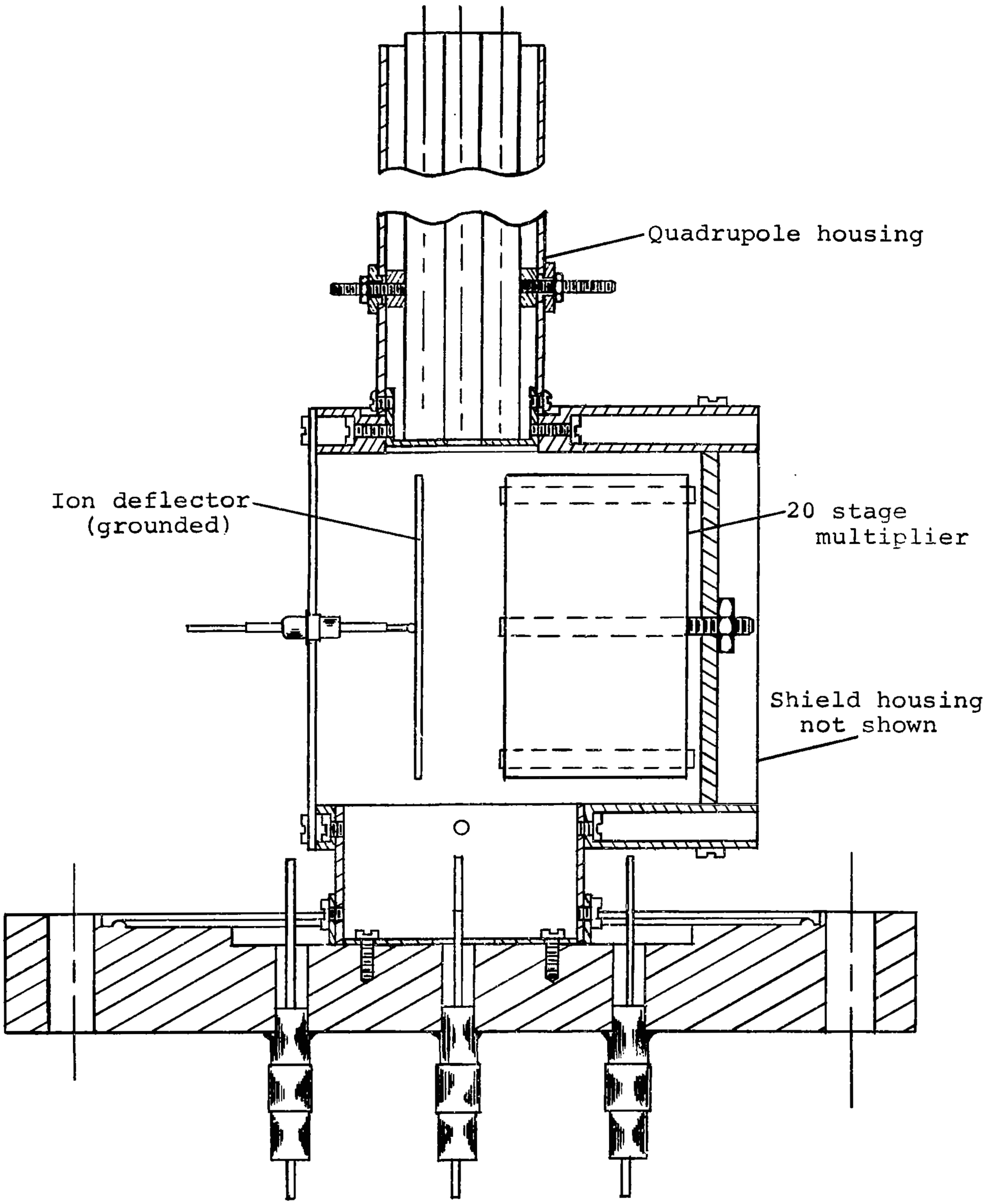

Figure 10.- 20 stage multiplier off-axis configuration

After mounting the multiplier as shown, rf interference problems were again encountered at the minimum discriminator setting. An unidentified intermittent noise source was also discovered which interrupted data acquisition despite line filters, etc. The rf interference would not permit digital spectra to be obtained for mass numbers larger than approximately 22 amu. The intermittent noise source completely masked photon noise rates. The collection efficiency for ions within the mass range 22-50 amu could not be measured because of these two noise sources. Despite these problems, the reduction of photon background in the off-axis configuration was successfully measured.

Figure 12 shows the counting plateau curve for mass 18 ions (most prominent peak) and demonstrates that under conditions similar to Fig. 6, all ions of mass 18 were being counted at 3000 volts on the multiplier. Since preamplifier overloading was again noted, data was not taken above 3200 volts. The lower portion of Fig. 12 also shows the total noise observed at 5.5 amu. This noise consists of electron multiplier dark noise and source photons. By subtraction, the net photon background is obtained. A value of approximately 70 counts per second is indicated. The photon background obtained in the on-axis configuration has been replotted from Fig. 6 data. A background rate of 3500 counts/sec is indicated from this data. The total discharge current for the off-axis data is approximately 30% less than that measured for the on-axis configuration. Therefore, the photon background obtained for the on-axis configuration should be reduced by approximately 30% before comparisons are made.

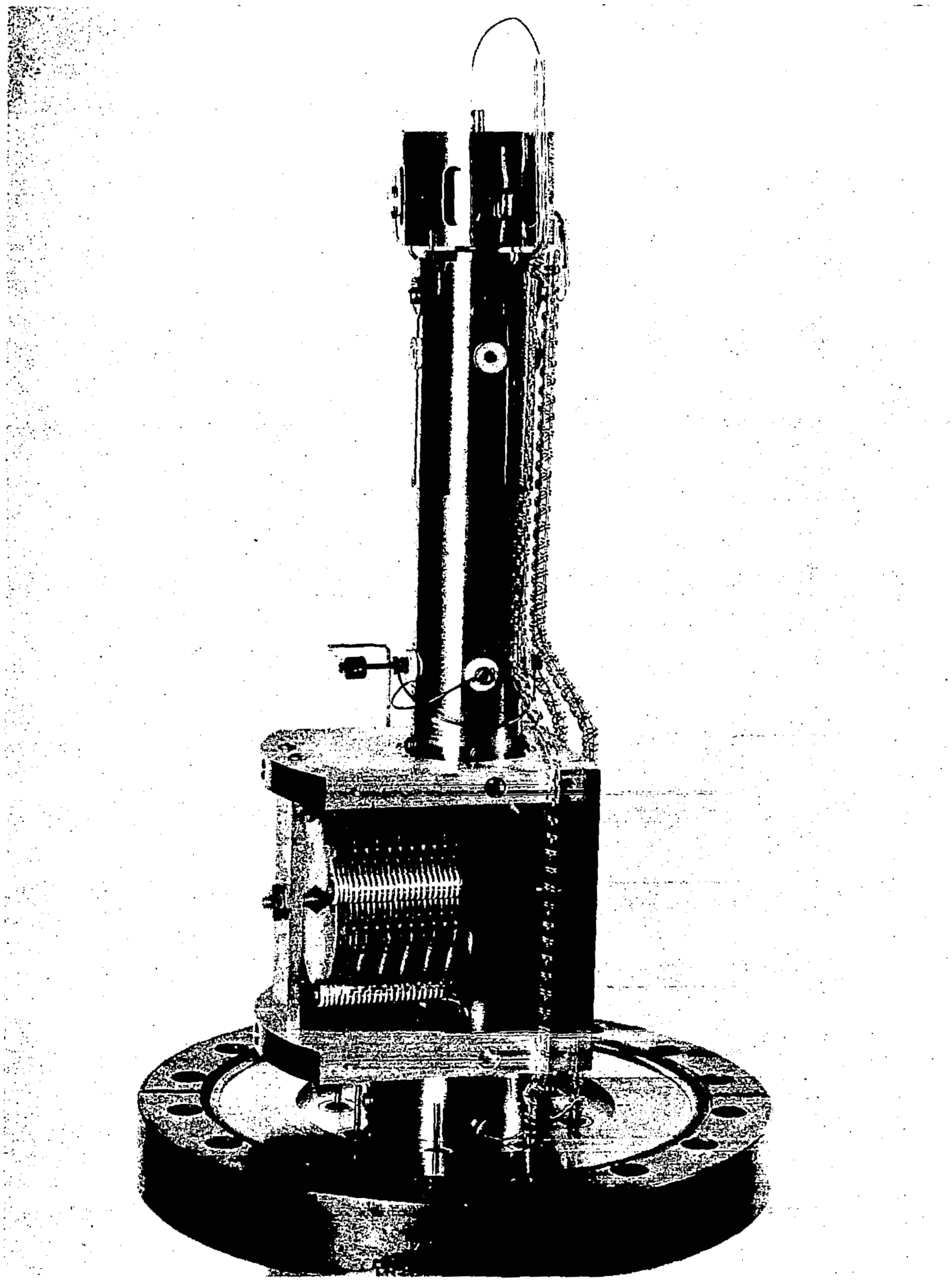

Figure 11.-Photograph of CCIS/Quad with off-axis, high gain multiplier.

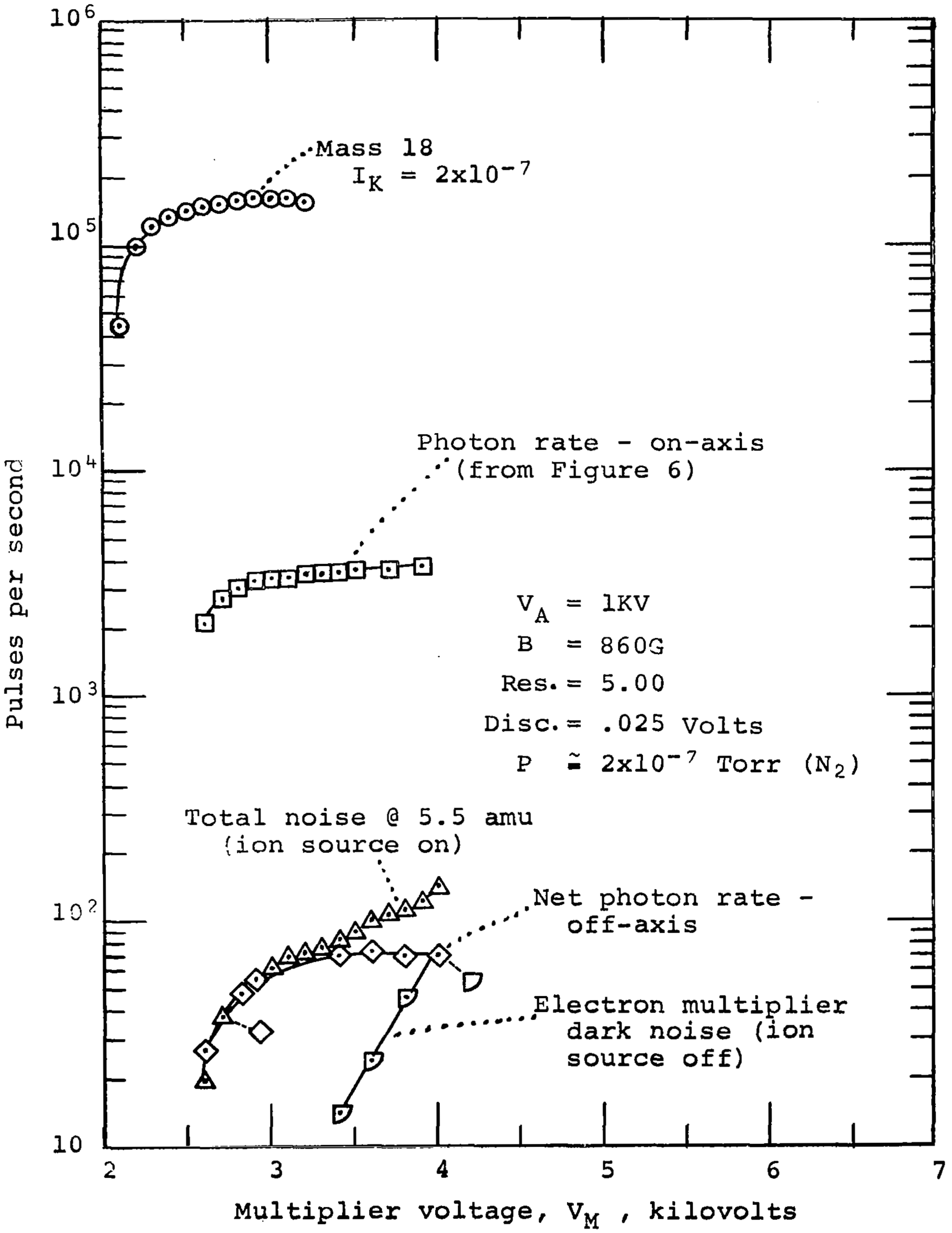

Figure 12.– Counting rate vs. multiplier voltage for 20 stage off-axis multiplier

Making this correction, the photon background on-axis would be 2460 counts per second. The off-axis background is approximately 70 counts per second. The reduction factor for the chosen configuration appears to be about 35. This compares with a factor of 300 obtained for the 14 stage multiplier. It is presently speculated that the difference in reduction factors is related to the first dynode entrance aperture areas. If photon scattering occurs it would be more pronounced in the larger area multiplier.

The final consideration of S/N ratio must involve the dark noise of the multiplier. The most expedient method of reducing this noise is by setting the discriminator to a value larger than the minimum used in the present studies. Attempts were made to obtain integral pulse height distribution curves of multiplier dark noise, photons and ions. The latter two distributions were readily obtained but reliable dark noise distributions could not be obtained below approximately a few counts per second because of the interference from outside noise sources mentioned earlier. Present data indicates that multiplier noise will be less than 1 count/sec at 3300 volts applied if the discriminator is set at 0.10 volts instead of 0.025 volts. The resultant reduction in counting efficiency for hydrogen would be only 1%. Therefore, with a minimal effect on counting efficiency (and detector stability), the S/N ratio of the spectrometer should be approximately 2×10^4 for nitrogen at 1×10^{-10} Torr. This figure is derived from the sensitivity calculated for nitrogen as shown in Fig. 4.

The final section of this report summarizes the conclusions drawn from the work described herein.

CONCLUSIONS

It has been shown that a very stable, high S/N ratio digital detector can be provided for the cold cathode ion source quadrupole mass spectrometer by choosing an appropriate high gain, low noise electron multiplier. Locating the multiplier off-axis effectively reduces the photon background from the ion source to a value which will not limit the spectrometer's UHV S/N ratio. The limiting internal noise source will be the dark noise in the multiplier itself, since this noise is not dependent on pressure.

The isolation of quadrupole rf noise and external laboratory noise from the detector is also of importance if the optimal S/N ratio is required for UHV mass spectrometry.

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